Devolatilization of Coal and Zinc Chloride - Impregnated
Coal in a Nitric Oxide Atmosphere

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Introduction

Zinc chloride acts as a catalyst for the hydrogenation of coal[1,2]. It has been proposed as a coal hydrogenation catalyst in a number of processes, but development of these processes has been hindered by corrosion and recovery problems of the zinc chloride. Zielke, et.al.[3,4] have reported on the catalytic activity of massive amounts of zinc chloride for hydrocracking coal, coal extracts and poly-nuclear aromatic compounds. Studies at the University of Utah[5,6] have shown the effectiveness of lesser amounts of impregnated zinc chloride for catalyzing coal hydrogenation. Conversions of up to 85% were obtained at residence times estimated to be one to six seconds. Dry coal was rapidly heated in an entrained-flow reactor. Coal is very reactive to hydrogenation in the presence of zinc chloride. However, the mechanism of catalysis is not understood and is an important and interesting problem for study.

Studies have shown that zinc chloride interacts with coal upon heating and produces important structural changes[7,8]. Pyrolysis of $ZnCl_2$-impregnated coals in inert atmospheres results in dehydrogenation of hydroaromatic groups in the coal and a decrease in the evolution of tars and gases. Hydrogen is evolved below 400°C when $ZnCl_2$ is present, but not in the absence of $ZnCl_2$. The hydrogen has been shown to come primarily from hydroaromatic groups. Dehydrogenation at relatively low temperatures results in supression of tar and gas evolution at higher temperatures. The acidic properties of zinc chloride on the coal surface disappear upon heating. Impregnated samples show large increases in surface area, enlargement of the capillary pores and hydrogen chemisorption properties upon heat treatment. The nature of intermediates formed by the $ZnCl_2$ during these reactions is of interest because of its possible roll in coal hydrogenation reactions. A Friedel-Crafts type acid intermediate has been proposed for hydrogenation with large amounts of zinc chloride[3]. In this report, the importance of free radical reactions is studied. Nitric oxide is used as a radical scavenger to terminate chain-propagation reactions.

Experimental

A microbalance was used to continuously record the weight of coal samples during heating at 5°C/min. and during isothermal experiments. Nitrogen or a 0.1 mole percent mixture of nitric oxide in nitrogen flowed through the reactor during the reaction at a rate of 0.2 l/min. Hiawatha, Utah coal was used in these experiments (high volatile bituminous, 43.1% VM on dry basis, 79.5% C, 5.2% H, 1.6% N, 0.6% S, 13.0% O). Impregnated samples were prepared by mixing coal with aqueous solutions of $ZnCl_2$ and evaporating the water[8].

Results and Discussion

Thermogravimetric analysis results are shown in figure 1. Hiawatha coal shows a typical weight loss curve in nitrogen atmospheres. The evolution of tar and gases is supressed by impregnation of 12% $ZnCl_2$. The effect of nitric oxide is to further decrease the loss of weight for both the coal and the impregnated coal. Above 500°C, there is considerable oxidation of the samples by the nitric oxide. The results of isothermal experiments at 400°C are shown in figure 2. A similar result is noted to that of the thermogravimetric analysis. The coal shows the loss of volatile matter in nitrogen atmospheres, while the impregnated coal shows a much

lower weight loss. The effect of the nitric oxide is to inhibit the pyrolysis reactions which lead to volatile products. The weight loss of the impregnated samples includes the loss of $ZnCl_2$. A result similar to that obtained with $ZnCl_2$ is obtained when $SnCl_2 \cdot 2H_2O$ is impregnated on the coal surface. Results of isothermal experiments are listed in table 1.

Table 1

Isothermal Weight Losses at 400°C

Sample	Atmosphere	Weight loss, %
Coal	N_2	27.5
Coal	NO/N_2	23.0
Effect of NO		4.5
Coal/12% $ZnCl_2$	N_2	14.3
Coal/12% $ZnCl_2$	NO/N_2	10.1
Effect of NO		4.2
Coal/20% $SnCl_2$	N_2	10.4
Coal/20% $SnCl_2$	NO/N_2	5.0
Effect of NO		5.4

Berkowitz and Dammeyer[9] studied the low-temperature carbonization of coal in the presence of nitric oxide and concluded that nitric oxide retarded thermal decomposition of the coal and inhibited secondary polymerization of tar when present at the start of pyrolysis. den Hertog and Berkowitz[10] reported an enhancement of decomposition due to nitric oxide. The partial pressure and flow rate of NO were much greater in these experiments.

Nitric oxide inhibits the devolatilization of coal, presumably by terminating free radical chain reactions. Zinc chloride and stannous chloride also inhibit the devolatilization of coal, but the effects of $ZnCl_2$ and $SnCl_2$ are independent of NO inhibition as shown in table 1. It can be concluded that $ZnCl_2$ and $SnCl_2$ reactions do not involve free radical chains in coal pyrolysis.

References

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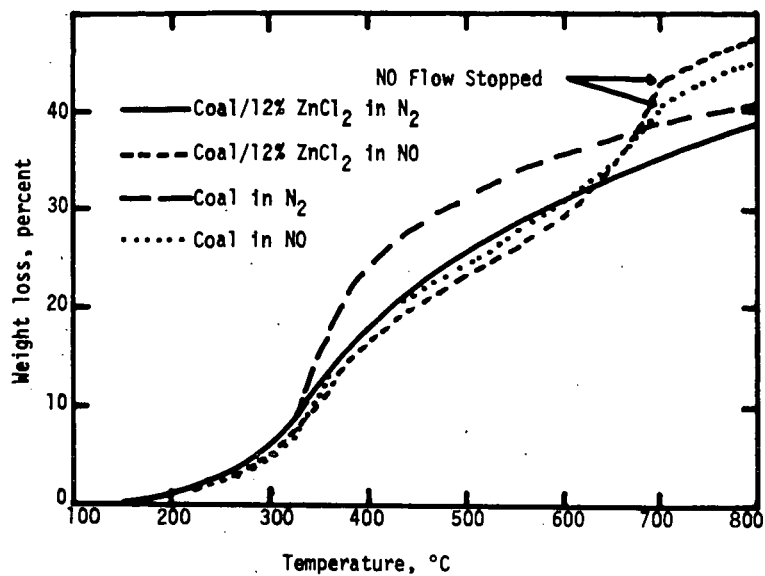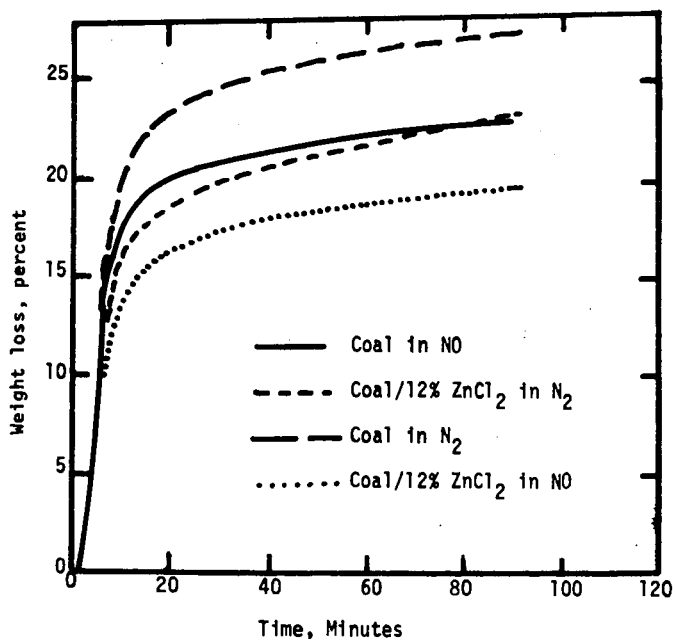10. den Hertog, W., and Berkowitz, N., Fuel, 39, 125 (1960).

Figure 1. Thermogravimetric Analysis

Figure 2. Isothermal Pyrolysis